Swami Ramanand Teerth Marathwada University, Nanded.

: Name of the Research Topic:

"Development and Characterization of Cu and Co Doped Nickel Oxide Thin Films for Gas Sensor Applications"

Faculty of Science in the subject of Physics

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1. Introduction

Metal oxide semiconductors (MOS) at the nanoscale have been widely focused because of its fast recovery time, excellent stability and high sensitivity. Metal oxide semiconductors are classified into n and p-type. Metal oxides are being studied for gas sensing applications [1]. Most of these studies have mainly been concentrate on n-type materials. An n-type metal oxide such as SnO_2, ZnO, In_2O_3, WO_3, Fe_2O_3 etc. have been sufficiently investigated over the year and most of the commercially available sensors are also based on n type metal oxides [2].

Presently, metal oxide semiconductors have been utilized to improve gas sensing properties of the MOS based gas sensors. Among them, incorporating transition metal dopants into MOS is considered to be most facile and reliable method to alter the structure from grain size, carrier concentration and distribution of oxygen components. Thus, promoting optical and gas sensing properties of MOS based devices [3]. Research interest in optical and gas sensing properties of pure and transition metal doped semiconductors such as NiO, CuO, Co_3O4 and Mn_3O_4 has been reasonable increased [4], [5]. NiO is one of the most important P type metal oxide semiconductors is used due to its wide band gap (3.6 eV) and excellent chemical stability. Among different oxide, the transition metal doped MOS such as NiO have an advantage of having very similar ionic radii of both electron and holes [6]. Therefore, NiO have attracted attention from scientific community. NiO thin films and nanostructures have been explore for their optical, electrical, and gas sensing properties. As a gas sensing material its sensitivity is relatively lower compared to n type metal oxide semiconductors. In addition, NiO possesses prominent catalytic activity for volatile organic compound oxidation [7].

Interestingly stoichiometric properties in NiO can be enhanced further by doing with transition metals such as iron, cobalt, Nickel, copper, silver which is mostly depends on method of sample preparation and experimental variables [8]–[11] Above mentioned factors affect the structural, optical, electrical and gas sensing properties which are of great importance for a basic understanding of transition metals doped NiO thin films. form this point of view NiO should be a potential material trace of designing and fabricating high-performance gas sensors. Hence some investigation into doping NiO thin films with transition metal ions to enhance gas sensing properties of NiO-based gas sensors have been carried out. Whereas for systematically

researching sensitization mechanism and realizing effective deduction of harmful and hazardous gases [12].

2. Literature Reviews

R. S. Kate et al. [13] deposited Co doped NiO thin films on a glass substrate using spray pyrolysis. Doping concentrations increased from 0 to 10%, affecting structural, morphological, and optical properties. X-ray diffraction confirmed polycrystalline nature with a cubic crystal structure. Co doping concentration increased band gap energies in range of 2.10 to 2.50 eV and modified optical constants.

Z. T. Khodair et al. [14] investigates copper-doped NiO nanostructures thin films prepared using chemical spray pyrolysis at 400°C. The films exhibit polycrystalline nature with a cubic structure, decreasing crystallite size with increasing copper concentration. XRD and AFM results show enhanced optical transmittance, increased absorption coefficient, and reduced optical energy gap for direct transmission.

A. Muzamil et al. [15] studied optical properties of undoped and Cu-doped NiO thin films deposited by spray pyrolysis. The absorption edge was within the UV range, with an average reflectance of 16.9%. As Cu/Ni ratio increased, the optical band gap decreased, while refractive index and Urbach energy increased. Optical conductivity was found to be 10^{14}-10^{15} s^{-1}, with low dielectric loss. The PL spectra showed an intense peak at 403 nm and two secondary peaks at 426 nm and 365 nm.

A. Diha et al. [16] investigated the impact of annealing temperatures (540, 560, 580, and 600 °C) on the synthesis of Co doped NiO thin films. The XRD analysis revealed a cubic structure with a high crystallite size of 82.57 nm at 580 °C, improving crystallinity. The optical transmission showed increased band gap energy and less disorder at high annealing temperatures. P-type semiconducting Co doped NiO films showed maximum electrical conductivity at 580 °C.

Y. E. Firat et al. [17] investigate electrochromic behavior of nanoporous Cu-doped NiO films in an alkaline medium, revealing improved optical modulation, coloration efficiency, and response time. The study also shows energy level diagrams and contributes to energy-saving smart windows development.

R. O. Ijeh et al. [18] synthesized Cu-doped NiO thin films using electrodeposition techniques, revealing polycrystalline, cubic structures with nanocrystalline grains. Optical and electrochemical studies showed decreased band gap energy, refractive index, and extinction coefficient values.

S. J. Mezher et al. [9] prepared Cu-doped NiO nanostructured thin films with various doping ratios. The structural properties studied using XRD and show cubic structure. The transmittance and energy gap decreased as copper doping ratio increased. The films showed increased sensitivity in Cu-doped NiO gas sensors for NO_2 and offer an economical p-type electronics production method.

L. Cattin et al. [19] prepared NiO thin films using chemical spray pyrolysis and studied their properties using precursors like nickel chloride hexahydrate, nitrate hexahydrate, hydroxide hexahydrate, and nickel sulfate tetrahydrate. Pure NiO thin films were achieved with $NiCl_2$ and Ni $(NO_3)_2$ precursors. The annealing process was found to be more efficient under vacuum, possibly due to oxygen interaction.

M. M. Gomaa et al. [20] created nickel oxide thin films using chemical spray pyrolysis on glass substrates. The films have a polycrystalline cubic structure, with a 3.4-3.5 eV optical direct band-gap energy and decrease in transmittance with deposition time. The films have a 57.3% sensitivity for nitrogen dioxide detection at 200°C, making them promising for low-temperature nitrogen dioxide detection.

3. Problem Under Study

NiO thin films are known for their unique properties, such as high electrical conductivity and optical transparency. These films have been widely used in applications such as gas sensors, solar cells, and electrochromic devices. In recent years, there has been a growing interest in the research and development of NiO thin films, with a focus on enhancing their performance and exploring new applications. This study aims to contribute to the existing knowledge by investigating the synthesis techniques, characterizing the properties, and exploring the potential applications of NiO thin films. By understanding the advantages and limitations of NiO thin film technology, we can further improve its performance and explore its potential in various fields.

4. AIM AND OBJECTIVES

a. To optimize deposition parameters

b. To Synthesize undoped, **Cu-doped,** and **Co**-doped **NiO thin film** by chemical route method.

c. To analyse the effect of Co and Fe doping on CuO thin films through structural, optical, and morphological properties.

d. To study the gas sensing characteristics of the undoped and doped NiO thin films

5. Motivation for Study

Cu-doped NiO thin films have gained significant attention in recent years due to their unique properties and potential applications. These films exhibit improved electrical conductivity, optical transparency, and catalytic activity, making them ideal for various technological advancements. Understanding the properties and behavior of Cu-doped NiO thin films is crucial for optimizing their performance and exploring new possibilities in areas such as energy storage, sensors, optoelectronics, and electrochromic devices.

Furthermore, Co doped NiO thin films have shown promise in applications such as electrochromic devices, where they can be used to control the transparency and reflectivity of windows and displays. Additionally, these films have the potential to be used in energy storage devices, such as batteries and supercapacitors, due to their enhanced conductivity and improved electrochemical performance. Thus, there is a strong motivation to study the relationship between Co doping concentration and film properties in order to optimize their performance in these diverse applications.

6. Methodology to be Used

- **Synthesis of the Thin Films**

NiO thin films can be produced using various processing techniques, including magnetron sputtering, dip-coating, electrodeposition, spray pyrolysis, chemical bath deposition, and sol-gel processes. Among this technique spray pyrolysis technique is the easiest, cost-effective, and powerful technique for large-area fabrication. Hence in the present investigation we use spray pyrolysis technique for the deposition of undoped and Cu-doped, and Co-doped NiO thin films.

- **Characterization Techniques**

  Various characterization techniques are employed to analyze the undoped NiO, Cu-doped NiO and Co-doped NiO thin films.

  i. **Structural Studies:** X-ray diffraction (XRD) is used to determine the crystalline structure and phase composition of the films. The structural parameters such as lattice parameters volume of unit cell, average crystal size, dislocation density, microstrain will be calculated from obtained XRD data of the films.

  ii. **Morphological Studies**: The surface morphology and elemental compositions of the samples were studied by filed effect scanning electron microscopy. Filed effect scanning electron microscopy (FE-SEM) provides information on the surface morphology and grain size of the films.

  iii. **Compositional Studies:** Elemental compositions of the samples were studied by electron diffraction spectroscopy (EDS). The correlation between taken composition and films composition will be obtained.

  iv. **Optical Studies**: Optical spectroscopy techniques, such as UV-Vis spectroscopy, are used to investigate the optical properties of the films, including optical transparency, absorption coefficient, and optical bandgap energy.

  v. **Gas Sensing Studies**: These characterization techniques provide valuable insights into the properties and performance of Cu and Co-doped NiO films, aiding in their potential applications.

Chapter Scheme

- Chapter 1: Introduction NiO Thin Films.
- Chapter 2: Experimental and Characterization Techniques.
- Chapter 3: Synthesis and Characterization of Cu-doped NiO Thin Films.
- Chapter 4: Synthesis and Characterization of Co-doped NiO Thin Films.
- Chapter 5: Conclusion and Future Scope.

Year Wise Plan and Targets to be Achieve

- **First year**

Completion of coursework in the first six month. During next sixth month a through literature review will be done to get knowledge of undoped and doped NiO thin films. Efforts

will be done to get good quality of undoped NiO, Cu-doped NiO and Co-doped NiO thin films by using spray pyrolysis method.

- **Second year**

In the second year the undoped NiO, Cu-doped NiO and Co-doped NiO thin films will be characterized by X-Ray Diffraction (XRD), Filed Emission Scanning Electron Microscopy (FE-SEM), Electron Diffraction Spectroscopy (EDS), UV-Vis spectrophotometer in order to study the structural, morphological, compositional and optical study.

- **Third year**

The obtained data in the second year will be analysis and results obtained will be communicated to the reputed journals for publication. Also result will be presented in national and international conference and seminars. Final synopsis and thesis will be submitted to university for the Doctoral degree.

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